

WE CLAIM:

1. A method for regenerating a deactivated iron-based Fischer-Tropsch catalyst from a slurry bubble column reactor, said method comprising the steps of:

placing a slurry comprising wax and deactivated catalyst into a first vessel;

feeding an inert gas into the bottom of the first vessel, thereby producing a three-phase bubble column in said first vessel wherein overhead gases are discharged to a separator;

removing a degassed catalyst and wax bearing slurry from an upper portion of the first vessel and allowing the degassed catalyst and wax bearing slurry to flow under natural circulation through a catalyst settling vessel into a lower portion of the first vessel, whereby said deactivated catalyst having undergone settling is returned to said first vessel;

adding an extraction solvent to said first vessel to maintain a desired level of catalyst bearing slurry as a catalyst-free wax and solvent mixture is removed from the catalyst settling vessel;

separating wax and solvent in said catalyst-free wax and solvent mixture in a flash vessel, thereby generating a separated wax and a recovery solvent;

recovering said separated wax;

returning said recovery solvent to said first vessel;

separating a dewaxed catalyst from the extraction solvent in said first vessel, thereby generating a wax-free catalyst-free solvent which undergoes vaporization and condensation for liquid storage;

oxidizing said dewaxed catalyst in said first vessel under controlled conditions;
mixing said dewaxed catalyst with a solvent containing an alkali promoter, thereby forming an oxide catalyst precursor;
drying said oxide catalyst precursor to form a catalyst precursor powder;
mixing said catalyst precursor powder with a liquid medium to form a catalyst precursor slurry; and
treating the catalyst precursor slurry with a synthesis gas to form an active catalyst containing iron carbides, thereby regenerating said deactivated catalyst.

2. The method as in claim 1 further comprising the step of removing said active catalyst from said first vessel.

3. The method as in claim 1, wherein the first vessel is a bubble column reactor.

4. The method as in claim 1, wherein the liquid medium further comprises wax or oil.

5. The method as in claim 1, wherein the deactivated catalyst is unsupported precipitated iron.

6. The method as in claim 1, wherein the inert gas is selected from the group consisting of nitrogen, carbon dioxide, and sulfur-free natural gas.

7. The method as in claim 1, wherein the extraction solvent is selected from the group consisting of hexane,

hexene, heptane, heptene, Fischer-Tropsch naphtha, and tetrahydrofuran.

8. The method as in claim 1 further comprising the step of heating the catalyst-free wax and solvent mixture entering said flash vessel to a temperature between about 125 and about 225°C.

9. The method as in claim 1, wherein said oxidation step further comprises an oxidation gas having between about 1 and about 5 percent by volume oxygen.

10. The method of claim 1, wherein said oxidation step further comprises a gas pressure between about 0.1 and about 0.7 MPaa.

11. The method of claim 1, wherein the oxidation step further comprises a gas temperature between about 200 and about 250°C.

12. The method of claim 1, wherein the activation step further comprises maintaining a slurry temperature of about 275°C for a length of time between about 2 and about 5 hours.

13. The method as in claim 1, wherein the step of feeding the inert gas into the bottom of the first vessel further comprises distributing gas bubbles in said inert gas uniformly across a cross sectional area of said first vessel.

14. The method as in claim 1 further comprising the step of recovering solvent present in said overhead gases.

15. The method of claim 1, wherein the synthesis gas has a $H_2:CO$ ratio between about 1.2 and about 1.4.

16. The method of claim 1, wherein the pressure of the first vessel is between about 0.8 and about 1.0 MPaa.

17. The method as in claim 1, wherein the deactivated catalyst is iron dispersed on a support.

18. The method as in claim 17, wherein the support further comprises aluminum oxide.

19. The method as in claim 17, wherein the deactivated catalyst further comprises potassium and copper.

20. The method as in claim 1, wherein the promoter is chosen from the group consisting of potassium, copper, magnesium, aluminum, and silicon.

21. The method as in claim 1, wherein the promoter is a mixture of potassium and copper.

22. The method as in claim 21, wherein the promoter also contains magnesium and aluminum.

23. A method for regenerating a deactivated iron-based Fischer-Tropsch catalyst from a slurry bubble column reactor, said method comprising the steps of:

placing a slurry comprising wax and deactivated catalyst into a first vessel;

intimately mixing an extraction solvent with the slurry at a superficial velocity above about 2.5 cm/sec;

extracting the wax from the slurry by passing a degassed catalyst bearing slurry through a catalyst settling vessel, whereby a catalyst-bearing slurry is returned to said first vessel, and by passing a catalyst-free wax and solvent mixture to a flash vessel for separating wax and solvent;

separating a wax-free catalyst from an extraction solvent in said first vessel;

oxidizing said wax-free catalyst in the first vessel under controlled conditions;

mixing said wax-free catalyst with a solvent containing an alkali promoter, thereby forming an oxide catalyst precursor;

drying said oxide catalyst precursor to form a catalyst precursor powder;

mixing said catalyst precursor powder with a liquid medium to form a catalyst precursor slurry; and

treating the catalyst precursor slurry with a synthesis gas to form an active catalyst containing iron carbides, thereby regenerating said deactivated catalyst.

24. The method as in claim 23, wherein the step of extracting the wax further comprises adding an extraction solvent to said first vessel to maintain a desired level of catalyst bearing slurry as the catalyst-free wax and solvent mixture is passed to the flash vessel.

25. The method of claim 23, wherein the first vessel is a bubble column reactor.

26. The method of claim 23 wherein the mixing step further comprises feeding an inert gas into the bottom of the first vessel.

27. The method as in claim 26, wherein the inert gas is selected from the group consisting of nitrogen, carbon dioxide, and sulfur-free natural gas.

28. The method of claim 23, wherein the degassed catalyst bearing slurry flows to the catalyst settling vessel by means of natural circulation.

29. The method of claim 23, wherein the catalyst-bearing slurry flows to the first vessel by means of natural circulation.

30. The method of claim 23 further comprising the step of recovering the extracted wax.

31. The method of claim 23 further comprising the step of returning solvent recovered from the flash vessel to the first vessel.

32. The method of claim 23, wherein the catalyst settling vessel is a dynamic settler.

33. The method as in claim 23 further comprising the step of removing said active catalyst from said first vessel.

34. The method as in claim 23, wherein the liquid medium further comprises wax or oil.

35. The method as in claim 23, wherein the deactivated catalyst is unsupported precipitated iron.

36. The method as in claim 24, wherein the extraction solvent is selected from the group consisting of hexane, hexene, heptane, heptene, Fischer-Tropsch naphtha, and tetrahydrofuran.

37. The method as in claim 23 further comprising the step of heating the catalyst-free wax and solvent mixture entering said flash vessel to a temperature between about 125 and about 225°C.

38. The method as in claim 23, wherein said oxidation step further comprises an oxidation gas having between about 1 and about 5 percent by volume oxygen.

39. The method of claim 23, wherein said oxidation step further comprises a gas pressure between about 0.1 and about 0.7 MPaa.

40. The method of claim 23, wherein the oxidation step further comprises a gas temperature between about 200 and about 250°C.

41. The method of claim 23, wherein the activation step further comprises maintaining a slurry temperature of about 275°C for a length of time between about 2 and about 5 hours.

42. The method as in claim 26, wherein the step of feeding the inert gas into the bottom of the first vessel further comprises distributing gas bubbles in said inert gas uniformly across a cross sectional area of said first vessel.

43. The method as in claim 23 further comprising the step of recovering solvent present in said overhead gases.

44. The method of claim 23, wherein the synthesis gas has a $H_2:CO$ ratio between about 1.2 and about 1.4.

45. The method of claim 23, wherein the pressure of the first vessel is between about 0.8 and about 1.0 MPaa.

46. The method as in claim 23, wherein the deactivated catalyst is iron dispersed on a support.

47. The method as in claim 46, wherein the support further comprises aluminum oxide.

48. The method as in claim 46, wherein the deactivated catalyst further comprises potassium and copper.

49. The method as in claim 23, wherein the promoter is chosen from the group consisting of potassium, copper, magnesium, aluminum, and silicon.

50. The method as in claim 23, wherein the promoter is a mixture of potassium and copper.

51. The method as in claim 50, wherein the promoter also contains magnesium and aluminum.

52. An apparatus useful for removing wax and impurities from a deactivated iron-based Fischer-Tropsch catalyst, said apparatus comprising:

extraction means functioning to extract wax from said deactivated catalyst in a catalyst bearing slurry using an extraction solvent in the presence of an inert gas;

said extraction means having a heating means functioning to heat inlet gases;

a first cooling means functioning to cool overhead gases from said extraction means;

a second cooling means functioning to condense solvent present in said cooled overhead gases;

a first separator means functioning to separate said cooled overhead gases from said condensed solvent exiting said second cooling means;

catalyst settler means functioning to produce a catalyst-free, wax-laden solvent mixture from said catalyst bearing slurry;

heating means functioning to increase temperature of the wax-laden solvent mixture before said wax-laden solvent mixture undergoes flash evaporation;

flash evaporator means functioning to separate solvent vapor from liquid wax in said wax-laden solvent mixture;

a third cooling means functioning to condense said solvent vapor discharged from said flash evaporator means;

a second separator means functioning to separate said condensed solvent from gases exiting said flash evaporator means;

solvent storage means functioning to store condensed solvent from said first and second separator means; and

wax storage means functioning to store liquid wax from said flash evaporator means.

53. The apparatus of claim 52, wherein said extraction means is a three-phase bubble column.

54. The apparatus of claim 52 further comprising pressure control means functioning to control pressure in said first vessel.

55. The apparatus of claim 52 further comprising flaring means functioning to dispose of tail gases from said first and second separator means.

56. The apparatus of claim 52 further comprising solvent pump means functioning to pump condensed solvent to said first vessel.

57. The apparatus of claim 52 further comprising wax pump means functioning to pump liquid wax from said wax storage means to a wax recovery system.

58. The apparatus of claim 52, wherein said extraction means further comprises gas distribution means functioning to distribute gas bubbles in said inert gas uniformly across a cross sectional area of said extraction means.

59. The apparatus of claim 58, wherein said gas distribution means is a sintered metal plate.

60. The apparatus of claim 59, wherein said sintered metal plate has an average pore diameter between about 0.2 and about 2 microns.

61. The apparatus of claim 52, wherein said extraction means further comprises a temperature control means functioning to maintain the catalyst bearing slurry at a desired temperature.

62. The apparatus of claim 52, wherein said catalyst settler means further comprises an external heating means functioning to maintain the catalyst bearing slurry at a desired temperature.

63. The apparatus of claim 52, wherein the catalyst settling means further comprises a dynamic settler.

64. An apparatus useful for separating a wax-free catalyst from an extraction solvent in a wax-free catalyst and solvent bearing solution after a wax extraction process and forming a dry catalyst powder, said apparatus comprising:

evaporation means functioning to vaporize said extraction solvent for discharge in an overhead gas, thereby removing said extraction solvent from said evaporation means;

condensing means functioning to condense solvent present in the overhead gas;

separation means functioning to separate said overhead gas from said condensed solvent exiting the condensing means;

solvent storage means functioning to store condensed solvent.

65. The apparatus of claim 64 further comprising solvent pumping means for pumping solvent to said evaporation means for another extraction.

66. The apparatus of claim 64, wherein said evaporation means further comprises a three phase bubble column.

67. The apparatus of claim 66 further comprising a gas distribution means functioning to distribute the inert gas uniformly across a cross sectional area of said three phase bubble column.

68. The apparatus of claim 67, wherein said distribution means is a sintered metal plate.

69. The apparatus of claim 68, wherein said sintered metal plate has an average pore diameter between about 0.2 and about 2 microns.

70. The apparatus of claim 64, wherein said solvent evaporation means further comprises a temperature control means functioning to maintain the wax-free catalyst and solvent bearing solution at a desired temperature.

71. The apparatus of claim 66, wherein the evaporation means used for solvent evaporation is the same as the extraction vessel used for extracting wax during the wax extraction process.

72. An apparatus useful for oxidizing wax-free deactivated iron-based FT catalyst back to an original Fe_2O_3 catalyst precursor state after a wax extraction process in an extraction vessel, said apparatus comprising:

vessel means functioning to contact said deactivated wax-free catalyst with an oxidizing gas to form a catalyst bed; and

heating means functioning to heat the vessel means, thereby heating the catalyst bed.

73. The apparatus of claim 72, wherein said vessel means for contacting said deactivated wax-free catalyst with said oxidizing gas further comprises a fluidized bed reactor.

74. The apparatus of claim 73 further comprising gas distribution means functioning to distribute said oxidizing gas uniformly across a cross section of said fluidized bed reactor.

75. The apparatus of claim 74, wherein said gas distribution means further comprises a plate means functioning to support the deactivated wax-free catalyst.

76. The apparatus of claim 75, wherein said catalyst bed is maintained at a temperature less than about 250°C .

77. The apparatus of claim 72, wherein said heating means further comprises an internal heat exchanger.

78. The apparatus of claim 74, wherein the vessel means used for contacting said deactivated wax-free catalyst with an

oxidizing gas is the same apparatus as the extraction vessel used for extracting wax during the wax extraction process.

79. An apparatus useful for contacting an oxidized catalyst with solution containing an alkali metal in the presence of an inert gas to form an oxidized catalyst precursor after a wax extraction process in an extraction vessel, said apparatus comprising:

vessel means for contacting said oxidized catalyst with said alkali metal containing solution to form a catalyst bed;

heating means functioning to heat the vessel means, thereby heating a catalyst bed; and

evaporation means functioning to evaporate said alkali metal containing liquid solution from said oxidized catalyst precursor.

80. The apparatus of claim 79, wherein said vessel means further comprises a three phase bubble column reactor.

81. The apparatus of claim 80 further comprising gas distribution means functioning to distribute a synthesis gas uniformly across a cross section of said bubble column reactor.

82. The apparatus of claim 81, wherein said gas distribution means further comprises a sintered metal plate.

83. The apparatus of claim 79, wherein said alkali metal containing liquid solution can be evaporated from said vessel means by raising the temperature until a dry catalyst powder is produced.

84. The apparatus of claim 80, wherein said bubble column reactor further comprises a heat exchanger.

85. The apparatus of claim 80, wherein the vessel means used for alkalizing the oxidized catalyst is the same apparatus as the extraction vessel used for extracting wax during the wax extraction process.

86. The apparatus of claim 80, wherein the evaporation means used for evaporating alkali metal containing liquid is the same apparatus as the extraction vessel used for extracting wax during the wax extraction process.

87. The apparatus of claim 82, wherein the sintered metal plate has a mean pore diameter between about 0.2 and about 2 microns.

88. An apparatus useful for activating an oxide catalyst precursor having undergone a wax extraction process and an oxidation process in a vessel, said apparatus comprising:

reactor means functioning to contact a wax/catalyst slurry with a synthesis gas;

heating means functioning to heat inlet gases of said reactor means;

gas cooling means functioning to cool overhead gases from said reactor means;

cooling means functioning to condense a liquid product in said overhead gases;

separator means functioning to separate said overhead gases from said condensed liquid product;

pressure control means functioning to control pressure
in said reactor means;
flaring means functioning to dispose of tail gases;
and
pressure control means functioning to control pressure
in said first vessel.

89. The apparatus of claim 88, wherein said reactor means further comprises a three phase bubble column.

90. The apparatus of claim 88 further comprising gas distribution means functioning to distribute a synthesis gas uniformly across a cross section of said reactor means.

91. The apparatus of claim 90, wherein the gas distribution means is a sintered metal plate.

92. The apparatus of claim 91, wherein the sintered metal plate has a mean pore diameter between about 0.2 and about 2 microns.

93. The apparatus of claim 89, wherein said three phase bubble column further comprises a heat exchanger.

94. The apparatus of claim 89, wherein the reactor means used for contacting synthesis gases with wax/catalyst slurry is the same apparatus as the extraction vessel used for extracting wax during the wax extraction process.

95. An apparatus useful for regenerating a deactivated iron-based Fischer-Tropsch catalyst from a slurry bubble column reactor, said apparatus comprising:

means functioning to remove wax and impurities from a deactivated iron-based Fischer-Tropsch catalyst;

means functioning to separate a wax-free catalyst from an extraction solvent in a wax-free catalyst and solvent bearing solution and to form a dry catalyst powder;

means functioning to oxidize said wax-free catalyst to an original Fe_2O_3 catalyst precursor state;

means functioning to contact said oxidized wax-free catalyst with solution containing an alkali metal in the presence of an inert gas to form an oxidized catalyst precursor; and

means functioning to activate said oxide catalyst precursor for use in a FT slurry bubble column reactor.